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Variation of photoabsorption cross section of atomic silver from isolated to condensed conditions*

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The influence of the local-field on the photoabsorption cross section of the atomic silver is studied in detail by using the Clausius–Mossotti (CM) model and the Onsager model separately. The variations of the photoabsorption cross section of atomic silver with number density and radius of the environmental interaction cavity are studied systematically by using more general expressions for the photoabsorption cross sections, proposed by Sun *et al* recently. It has proved to be reasonable to model the optical response properties of bulky material by coupling the property of isolated atom with the environmental effects in the present work.

Keywords: condensed-phase photoabsorption, local field, dielectric constant, silver
PACC: 3280F, 3280, 3380E

1. Introduction

As the Dalton's postulation states, atoms retain their own identity even in chemical combinations with other atoms. The optical response properties of materials are to a large extent governed by the properties of individual atoms and to some extent by the interactions with the neighbouring atoms.[1] Therefore, the isolated atomic response properties and the perturbations caused by the environmental interactions both are needed in order to understand and interpret the response property of the bulky materials. However, most of the present theoretical methods have been used to attempt the quantum-mechanical *ab initio* calculations directly on the entire of the condensed system. From the theoretical point of view, the quantum-mechanical *ab initio* method can be applied to describing these sophisticated systems accurately, but in reality, these *ab initio* methods can be carried out accurately only for some small molecules, especially for the isolated atoms. For bulky material systems, it is still very difficult to perform the complete quantum-mechanical *ab initio* calculations nowadays due to a requirement for large computer resources. However, the property of the individual atoms can be calculated accurately and easily by using the quantum mechanical *ab initio* method or obtained experimentally. The environmental influence on the photoabsorption cross section in the condensed matter might be modelled by using some local field models with electron overlap effects, the dipole-dipole interactions, the multipole interactions,[2−7] etc., therefore, coupling the isolated atomic properties with the environmental effects would open a simple way to understand the response properties of multiatomic systems. From this very simple view, once the accurate photoabsorption cross section of the isolated atom has been obtained, the variation of the photoabsorption cross section from the isolated state to the condensed conditions or multiatomic systems then can be represented by different local field effects directly.

The influence of the interatomic interactions in the condensed environments or at high density or at high temperature on the photoabsorption cross section has been a main research subject of the condensed physics and the chemical physics.[8−11] In the present work, the variations of the photoabsorption cross section of atomic silver with number density in the different local field models under the Onsager model are studied by using the new expressions of photoabsorption cross sections. These expressions can couple the photoabsorption cross sections of the isolated atoms with the environmental effects directly and can just realize the above view. The element silver is always applied to the simulation experiments of the inertial confinement fusion due to its good conduction of heat and

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the high efficiency of the generation of the hard x-ray converted from the interactions with the laser. So the photoabsorption cross sections of silver under different conditions such as at high density, at high temperature, etc., are urgently needed in these experiments. However, most of the studies for the photoabsorption cross sections of the atomic silver in ordinary states, such as the isolated atoms,[12] solid silver,[13−16] and many compounds and clusters of silver are performed experimentally. Some of these studies have been summarized by Henke *et al.*[17] There is almost no theoretical result obtained especially by using the complete quantum mechanical *ab initio* method for photoabsorption cross sections of the atomic silver systems due to the limitation of the computer resources. The variation of the photoabsorption cross section of the atomic silver from the isolated state to the solid, compound and cluster states has already become an important research subject for the physical theorists and experimentalists. Obviously the quantum mechanical *ab initio* calculations cannot be carried out due to complexities and only the theoretical calculations with the help of some interaction models can be performed for these systems. In the present work, we try to combine the accurate isolated atomic properties with local field models of the system to study the variation of the photoabsorption cross section of silver from the isolated state to the condensed state in a unique way.

2. Coupling isolated atoms with the modelled environments

The photoabsorption cross sections for isolated atoms and molecules can be calculated usually by using the well-known expression[18]

$$\sigma_i(\omega) = \frac{4\pi\omega}{c}\zeta = \frac{4\pi\omega}{c}\mathrm{Im}(\alpha), \tag{1}$$

where ζ is the imaginary part of polarizability $\alpha(\omega)(= \eta + \mathrm{i}\zeta)$ of atom, and ω is the photon energy. In order to study the influence of the macroscopic local field on the photoabsorption cross section, one should couple the macroscopic effect and the photoabsorption cross section of an isolated atom, as expressed below:[19]

$$\sigma(\omega) = \mathrm{DIF} \times \sigma_i(\omega), \tag{2}$$

where $\sigma(\omega)$ represents the cross section of an atom embedded in some condensed matter, while $\sigma_i(\omega)$ denotes the cross section of the same atom which is isolated or in an ideal gas. The influence of the surrounding atomic interactions with the photo-ionized atom on the photoabsorption cross section can be easily investigated by using the so-called dielectric influence function (DIF)[19]

$$\mathrm{DIF} = \frac{1}{2\sqrt{2}\pi N\zeta}\sqrt{\sqrt{\varepsilon'^2 + \varepsilon''^2} - \varepsilon'}, \tag{3}$$

where N is the number density and $\varepsilon(= \varepsilon' + \mathrm{i}\varepsilon'')$ is the complex dielectric function. Expression (2) will be identical with Eq.(1), if an atom in an ideal gas and only the first order of the series expansion of Eq.(3) are taken into consideration.

In the present work, the influence of the macroscopic local field on the photoabsorption cross sections in the Clausius–Mossotti model and the Onsager model has been investigated separately in detail by using the above method. Nowadays, the accurate photoabsorption cross section σ_i of the isolated atom can be easily obtained by using some quantum mechanical *ab initio* methods or from some experimental databases. In order to obtain the photoabsorption cross section σ of atom embedded in a medium from the σ_i of the isolated atom, one must know the relation between the dielectric constant of matter and the polarizability of atom according to expression (3). These relations can be obtained by using some local field models. For most of the liquids and some simple solids, the dielectric constants ε can be related to atomic polarizabilities by using the Clausius–Mossotti (CM) model and expressed as

$$\varepsilon = 1 + \frac{4\pi N\alpha}{1 - 4\pi N\alpha/3} \tag{4}$$

and by using the Onsager model and expressed as

$$\varepsilon = 1 + 4\pi N\alpha\frac{3\varepsilon}{2\varepsilon + 1 - 2\alpha/r^3(\varepsilon - 1)}, \tag{5}$$

separately. The variable r in expression (5) can be taken as the interaction radius of local cavity, and usually it is taken as the distance between atoms.

The imaginary part ζ and the real part η of polarizability can be calculated in practice from the photoabsorption cross section $\sigma_i(\omega)$ of ideal gas or isolated atom as

$$\zeta(\omega) = \frac{c}{4\pi\omega}\sigma_i(\omega), \qquad \omega > 0 \tag{6}$$

and from the Kramers–Kronig relation as

$$\eta(\omega) = \frac{c}{2\pi^2}\mathrm{P}\int_0^\infty \frac{\sigma_i(\xi)}{\xi^2 - \omega^2}\mathrm{d}\xi \tag{7}$$

respectively, where the variable ξ is also the photon energy and P indicates the Cauchy principle part of

the integral. The main obstacle to the practical application is that the Hilbert transform in expression (7) must be performed over infinite limits. However, the measurements provide values of photoabsorption cross section σ_i only over some finite frequency range. Truncation of the integration in the computation of the Hilbert transform expression (7) can yield a computational error in calculating the real part in the measured frequency range. At the same time it is also difficult to analyse the error introduced from the Hilbert transform in expression (7). This problem cannot be solved thoroughly unless the missing photoabsorption cross sections are supplied. In order to avoid the computational error introduced by expression (7), we use the Lorentz model of the polarizability in which the real part and the imaginary part of polarizability satisfy the Hilbert transform instead of the infinite integral. If the photoabsorption cross section σ_i of the isolated atom is given, one can calculate the corresponding imaginary part of polarizability by using expression (6), and then use the Lorentz function as the basis function to fit the known imaginary part[20]

$$\zeta(\omega) = \frac{c}{4\pi\omega}\sigma_i(\omega) = \sum_{i=1}^{M} \frac{A_i}{\pi} \cdot \frac{\frac{\gamma_i}{2}}{(\omega - \omega_{Ti})^2 + \left(\frac{\gamma_i}{2}\right)^2}. \tag{8}$$

M sets of parameters ($A_i,\ \omega_i,\ \gamma_i$) can be determined then. Substituting these M sets of parameters into

$$\eta(\omega) = \sum_{i=1}^{M} \frac{A_i}{\pi} \cdot \frac{-(\omega - \omega_{Ti})}{(\omega - \omega_{Ti})^2 + \left(\frac{\gamma_i}{2}\right)^2} \tag{9}$$

for a given ω, one can obtain the corresponding real part of the polarizability.

The most important innovation of these new expressions is coupling the local field effects with the isolated atomic properties distinctly. Using this general expression of the photoabsorption cross section, the variation of the photoabsorption cross section from the isolated state to the condensed state can be easily investigated. However, there are still two important factors which can influence the accuracy of the theoretical results greatly. One of them is the accuracy of the local field model for the actual multiatomic systems. The more correct the local field model of the condensed matter is, the more accurate the photoabsorption cross sections obtained from this expression will be. The other is the influence of the integral instability of the Kramers–Kronig transformation on the photoabsorption cross section. Although the present algebraic fitting process, instead of the integral process, can work well, the accuracy of the photoabsorption cross section will be very sensitive to the fitting process: sometimes the theoretical results are wrong thoroughly. Searching for more correct local field model and more accurate integral method for Kramers–Kronig transformation is the key point to use these alternative expressions.

3. Application and discussion

The imaginary part of the polarizability of atomic silver has been obtained directly by using the photoabsorption cross section[17] of the experimental ideal gas from expression (6). The real part of the atomic polarizability can be calculated by using several methods. In our previous calculations for the atomic silver,[19,21] the real part of the polarizability has been calculated from expression (7) by using some Kramers–Kronig transformation codes with the direct truncation of the integral in some limited interval. Some result[21] are in good agreement with the measurements. However, the real parts of the polarizability calculated usually by using the famous Kramers–Kronig transformation from the photoabsorption cross sections of the isolated atoms are very sensitive to the implementation method of the infinite integral.[20] One cannot determine how reliable these calculations are. Especially in the high density conditions, the variation of the photoabsorption cross section with number density is always sensitive to the sign of the real part of the polarizability. Usually the different model functions used in the interpolation process for the integrand will give out the different signs of the infinite integral. In the present work, the real part of polarizability is determined by Eq.(9) with parameters which are obtained through performing the multiparameter least-squares fitting to the experimental imaginary part of the polarizability.[20] The present procedure will avoid the errors originating from the Kramers–Kronig transformation. In this section, we study the variation of the photoabsorption cross section of atomic silver from the isolated state to the condensed condition in the Clausius–Mossotti model and the Onsager model. For some simple solids and most of the liquids, these models have proven to be very good to describe the local fields around the target atoms.

Figure 1 shows the present theoretical photoabsorption cross section in a photon energy region of

30–200 eV in the CM model with the number densities varying from $1.0 \times 10^{-6} a_0^{-3}$(corresponding to an ideal gas condition) to $1.0 \times 10^{-1} a_0^{-3}$(even larger than the number density of the solid silver). The complex dielectric constant $\varepsilon(= \varepsilon' + \mathrm{i}\varepsilon'')$ in expression (4) can then be calculated from the above complex atomic polarizability with different number densities. A great change of the photoabsorption cross section with number density occurs in an energy region below 125 eV compared with the experimental photoabsorption cross section of the ideal gas. In a region above 125 eV, there is almost not any variation of the photoabsorption cross section as number density increases except in the highest density condition where there is no physical meaning for silver atoms. So one should pay attention only to the change law of the photoabsorption cross section with number density in an energy range below 125 eV. In this energy region, the number density is below about $0.03 a_0^{-3}$, and the photoabsorption cross section increases smoothly as number density increases from $10^{-6} a_0^{-3}$ to $10^{-4} a_0^{-3}$. Then, as the number density increases continuously, the variation begins to increase dramatically and at about $0.03 a_0^{-3}$, the photoabsorption cross section at the lowest energy reaches a maximum. Then the photoabsorption cross section begins to decrease dramatically but it is still larger than that of the ideal gas in a low energy region. Finally as number density reaches about $0.04 a_0^{-3}$, the photoabsorption cross section in the whole energy region is less than that of the ideal gas and will not vary any more. The change law of the photoabsorption cross section with number density in the CM model has also been studied in our previous work.[7,21] But the real part of the polarizability has been calculated by the truncation of the integral of expression (7). The behaviour is very different from that of the present results and that variation is the most like that of the highest number density part of the present behaviour in an above $0.03 a_0^{-3}$ energy region. So the change law of the photoabsorption cross section is very sensitive to the way of performing the Kramers–Kronig transformation infinite integral. Unfortunately, the different ways of executing the Kramers–Kronig transformation will give very different real parts, which can significantly affect the variation of the photoabsorption cross section with number density especially in the case of higher number density. The Kramers–Kronig transformation infinite integral is a bottleneck in applying these general expressions to the study of the condensed-phase photoabsorption processes. Some more accurate implementations of Kramers–Kronig transformation and self-consistent procedures for the complex atomic polarizability must be needed urgently in our present and future studies.

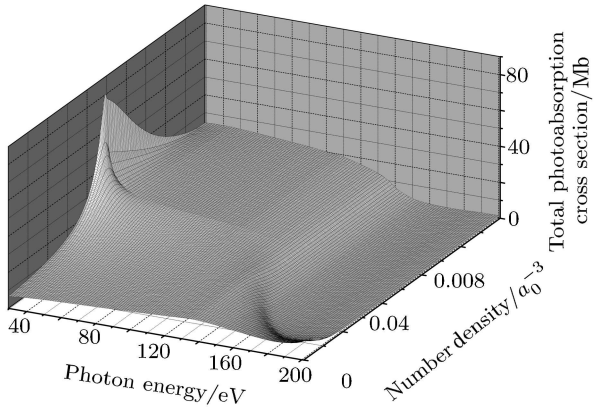


Fig.1. Variation of the energy-dependent photoabsorption cross section of atomic silver with number density in the Clausius–Mossotti model.

The variation of the photoabsorption cross section with number density in a range from $1.0 \times 10^{-6} a_0^{-3}$ to $2.0 \times 10^{-2} a_0^{-3}$ in the Onsager model with the cavity radius $r = 5.46 a_0$ is shown in Fig.2. The radius of the interaction cavity is taken from the bond length in AgAg[22] which can be considered as the average spacing between Ag atoms in solid. Surprisingly for the same real and imaginary parts of the atomic polarizability, the general variation of the photoabsorption cross section at a glance is very different from the behaviour in the CM model. In order to analyse the variation of the photoabsorption cross section with number density, one can divide the whole energy region into three parts. For the lowest energy region, as number density increases, the photoabsorption cross section decreases continuously and slowly. In the second energy region, i.e. the resonance peak of the photoabsorption cross section, the details of the variation in this region are essentially different in these two models. At the same time, one can notice that the DIF can strongly affect only the photoabsorption cross section near the resonance structure in the Onsager model. In this resonance region, the photoabsorption cross section becomes larger and larger as number density increases. The resonance position also shifts toward the higher energy region and the width of the resonance becomes more and more broad as number density increases. This accords with the actual phenomena in condensed matters, such as line broadenings and spectral shifts of optical spectra of atoms in condensed

states which contain the information on both the dynamics of liquid and the interatomic interactions. In the region far from the resonance, the photoabsorption cross section decreases slowly as number density increases, and in the highest energy region, the local field has almost no effect on the photoabsorption cross section any more. Compared with results obtained in the CM model, the results acquired in the Onsager model are much close to those obtained from solid experiments and show the correct behaviour that is dependent on actual condition of the experiments. The resonance peak in the CM model shifts toward the lowest energy region and the width becomes narrower and narrower as number density increases. This behaviour is opposite to the actual phenomena in condensed matters, and obviously it is wrong. Using these two models yields the theoretical results that are almost the same as the results obtained from ideal gas experiment in number density of the ideal gas. That is to say, the CM model and the Onsager model are both convergent to the ideal gas model as number density approaches to that of the ideal gas.

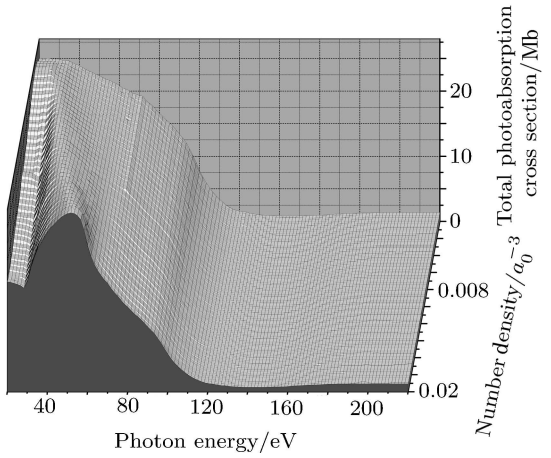


Fig.2. Variation of the energy-dependent photoabsorption cross section of atomic silver with number density in the Onsager model with $r = 5.46a_0$.

In Fig.3, we present the results where the photoabsorption cross section is varying with radius of cavity or spacing between atoms in a range from $0.1a_0$ to $10a_0$ at the number density of solid $N = 8.69 \times 10^{-3}a_0^{-3}$ in the Onsager model. The size of the radius of cavity represents in general the magnitude of the interactions between atoms in a condensed matter. The theoretical study shows that in a higher photon energy region, about in 160–200 eV for silver, these interactions have almost no effect on the photoabsorption cross section of the ideal gas and the photoabsorption cross section almost does not depend on cavity radius any more. In the lower photon energy region, near the resonance structure and the threshold region, the characteristic of the variation of the photoabsorption cross section along the radial direction can be sorted into three parts. When the radius of the cavity is larger than about $6a_0$, the photoabsorption cross section varies very weakly as the radius decreases from $10a_0$. This is because for these spacings between atoms, the interactions are very weak and have almost no local field effect on the photoabsorption cross section. But when the radius is greater than $6a_0$, about in a region of $6a_0 - 2a_0$, the photoabsorption cross section changes quickly as the radius varies from $6a_0$ to $2a_0$ and reaches a maximum at about $3a_0$. Then the photoabsorption cross section decreases dramatically in a lower energy region from $3a_0$ to $2a_0$. When the radius is less than $2a_0$, the photoabsorption begins to decrease slowly in the lower photon energy region and begins to increase in the higher energy region as the radius continuously decreases. Finally, for the smallest radius, the photoabsorption in the whole energy region does not vary with photon energy any more. As the radius of cavity decreases, i.e. the interactions between atoms become more and more strong, the theoretical result in low energy region will become decreasing and more and more close to the case of solid experiment. The variation of the photoabsorption cross section with radius follows the same law as the variation of the photoabsorption cross section with number density. As the radius decreases, the interaction between atoms becomes more and more strong, and the photoabsorption cross section in the threshold energy region will be more and more close to the case of solid experiment in solid number density and radius.

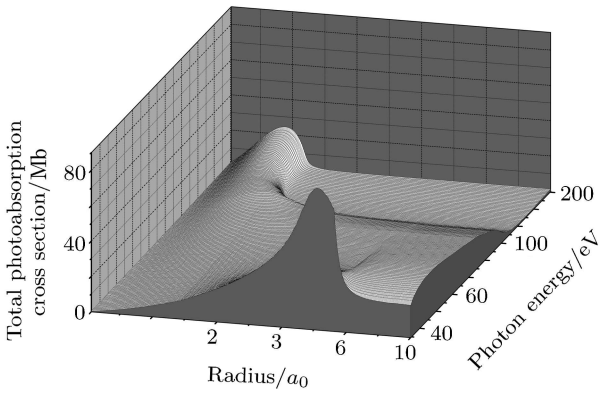


Fig.3. Variation of the energy-dependent photoabsorption cross section of atomic silver with radius of cavity in the Onsager model with $N = 8.69 \times 10^{-3}a_0^{-3}$.

In Fig.4, the photoabsorption cross sections of the ideal gas experiment, denoted by symbol "×",[17] and those from the solid phase experiment, represented by symbol "○",[13] are compared with the present theoretical results. These theoretical results are calculated from the same atomic polarizabilities which are calculated from the ideal gas experimental data and Kramers–Kronig transformation through using our general expressions in the CM model and the Onsager model separately. All of these theoretical photoabsorption cross sections will be convergent to the gas experimental results denoted by symbol "×" in the ideal gas number density shown in the foregoing figure. In the number density $N = 8.69 \times 10^{-3} a_0^{-3}$ of solid silver, the theoretical photoabsorption cross sections in the CM model are not considerably different from those obtained from the ideal gas experiments. When the number density is larger than that of solid state, the CM theoretical results begin to have the same structures as those from the solid experiments. For the Onsager model with the radius$r = 5.46a_0$, as number density increases, the position of the resonance shifts toward the higher energy region and the width becomes broader and broader. At the solid number density, when the radius of cavity becomes small, for example, $r = 1.50a_0$, the results obtained in the Onsager model are in good agreement with the measurements from the solid experiments and have almost the same behaviour as the results obtained in the CM model at $N = 4.69\times10^{-2}a_0^{-3}$. Compared with the results obtained in the CM model, the results obtained in the Onsager model are close to those obtained from the solid experiments and show the correct behaviour that is dependent on the actual experimental condition. The Onsager model is even more correct than the CM model in solid number density. However the difference between the theoretical results and the measured results from solid experiments is still large. This indicates that the interactions in the cavity could not represent all of the interactions acting on the photoabsorption atoms and more local field effects should be considered.

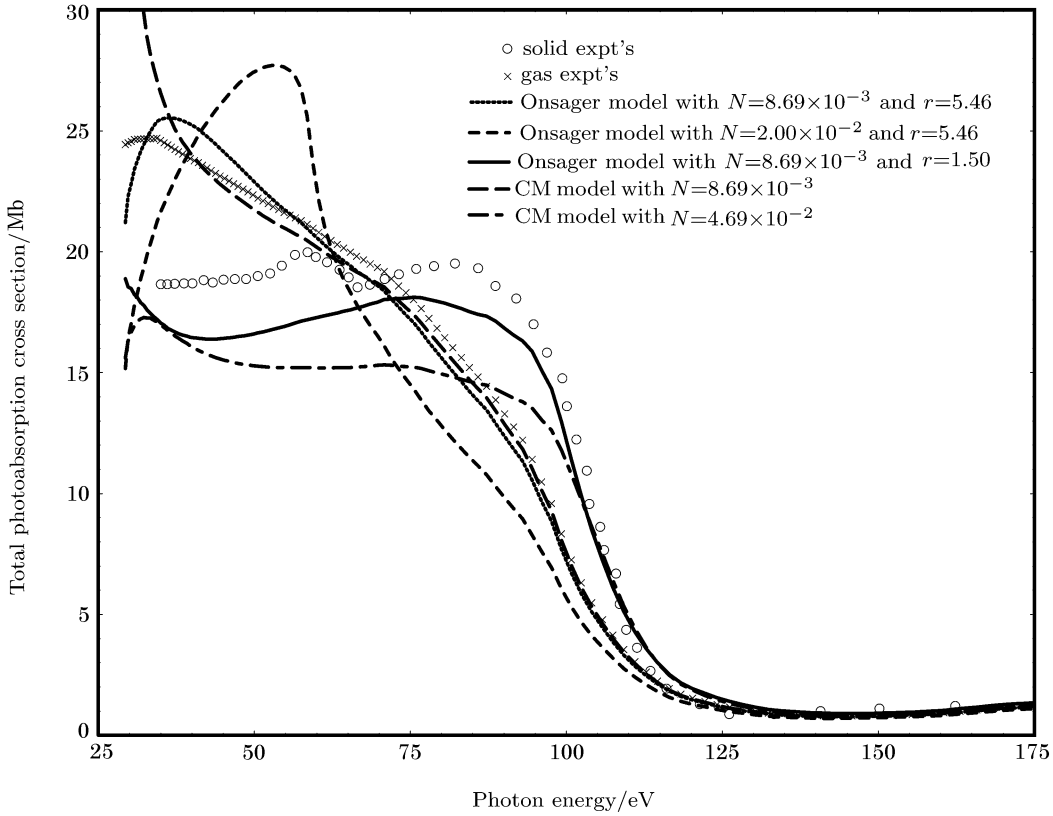


Fig.4. Comparisons between photoabsorption cross sections obtained from the ideal gas experiment and the solid phase experiment and the present theoretical results.

4. Conclusion

In the present work, the variations of the photoabsorption cross section of atomic silver with number density and radius of cavity of macroscopic local field model are studied. All of these models involved in the present paper can be applied successfully to calculating the photoabsorption cross sections of atoms under ideal gas condition. This is because the expression of the photoabsorption cross section of atom in a medium will converge to the expression of isolated atom, i.e. expression (2) approaches to expression (1), when the number density tends to that of an ideal gas. This indicates that the present expression (2) for the photoabsorption cross section is reasonable and more general than expression (1). The well-known expression (1) is only the first-order approximation of expression (2) and can be applied only to the isolated atoms or an ideal gas. When the number density is greater than that of the ideal gas, the law of photoabsorption cross section varying with number density is different from those for different local field models. The general expression gives out the correct variation of the photoabsorption cross section of atomic silver from the isolated state to the condensed matter. The present study not only can give a new reasonable way to study the condensed photo-ionization and excitation processes of atoms in special conditions at atomic and molecular levels, but also can obtain the accurate models and data which will be used in some other important scientific researches.

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References

[1] Jensen L, Astrand P O, Osted A, Kongsted J and Mikkelsen K V 2002 *J. Chem. Phys.* **116** 4001
[2] Sole R Del, Mochan W L and Barrera R G 1991 *Phys. Rev.* B **43** 2136
[3] Schmidt W G and Bernholc J 2000 *Phys. Rev.* B **61** 7604
[4] Rodolfo Del Sole and Giovanni Onida 1999 *Phys. Rev.* B **60** 5523
[5] Sun W G, Ma X G and Cheng Y S 2004 *Phys. Lett.* A **326** 243
[6] Ma X G, Sun W G and Cheng Y S 2005 *Commun. Theor. Phys.* **43 159**
[7] Ma X G, Sun W G and Cheng Y S 2005 *Acta Phys. Sin.* **54** 1149 (in Chinese)
[8] Jansen T I C, Swart M, Jensen L, Duijnen P T and Snijders J 2002 *J Chem. Phys.* **116** 3277
[9] Zangwill A and Soven P 1980 *Phys. Rev.* A **21** 1561
[10] Kanik I, Beegle L, Noren C, Ahmed S M and Link R 1997 *Chem. Phys. Lett.* **279** 297
[11] Yenen O, McLaughlin K W, Jaecks D H, Sant Anna M M and Seddon E A 2001 *Phys. Rev. Lett.* **86** 979
[12] Andrews C L 1938 *Phys. Rev.* **54** 994
[13] Haensel R, Kunz C, Sasaki T and Sonntag B 1968 *Appl. Opt.* **7** 301
[14] Hagemann H J, Gudat W and Kunz C 1975 *J. Opt. Soc. Am.* **65** 742
[15] Lurio A and Reuter W 1975 *Appl. Phys. Lett.* **27** 704
[16] Windt D L, Cash W, Scott M, Arendt R, Newnam B, Fisher R F and Swartzlander A B 1988 *Appl. Opt.* **27** 246
[17] Henke B L, Gullikson E M and Davis J C 1993 *At. Data Nucl. Data Tables* **54** 181
[18] Fano U and Cooper J W 1968 *Rev. Mod. Phys.* **40** 441
[19] Ma X G 2006 *Phys. Lett.* A **348** 310
[20] Ma X G, Gong Y B, Wang M S and Wang D H 2008 *Phys. Lett.* A **372** 2274
[21] Ma X G and Sun W G 2005 *Chin. Phys.* **14** 1792
[22] Sutton L E (ed.) in *Table of Interatomic Distances and Configuration in Molecules and Ions* Supplement 1956–1959, Special Publication No.18 (London: Chemical Society) 1965